EFFECT OF THE CONSOLUTE POINT OF

ISOBUTYRIC ACID + WATER ON THE RATE OF

AN S_N1 HYDROLYSIS REACTION[1]

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ABSTRACT

The rate constant for the S_N1 hydrolysis of 2-chloro-2-methylbutane was measured near the consolute point of the liquid mixture isobutyric acid + water. At temperatures far from the upper critical solution temperature, T_c, of this mixture, the rate constant obeyed the Arrhenius equation. In the one-phase region just above T_c, however, the rate constant decreased below the Arrhenius background, while in the two phase region below T_c it increased. This combination of slowing down with speeding up appears to be beyond the scope of explanation of the current theories of dynamic critical slowing down.

1. INTRODUCTION

The consolute point is an extrenum in the temperature vs. mole fraction phase diagram for a binary mixture where the homogeneous liquid solution first begins to separate into two immiscible liquid layers. See Fig. 1. A mixture of two components having a liquid-liquid phase boundary in this variable space that is concave down is said to have an upper critical solution temperature (UCST). The UCST is the minimum temperature above which the two liquids are miscible in all proportions. A liquid-liquid phase boundary that is concave up is described as having a lower critical solution temperature (LCST). The LCST is the maximum temperature below which the liquids are miscible in all proportions.

Binary liquid mixtures can be used as solvents for chemical reactions. The consolute point of the liquid mixture at one atmosphere pressure and the liquid-vapor critical point of a pure fluid are members of the same universality class [1]. This implies that the consolute point can be exploited to study the effects of thermodynamic criticality on the rates of chemical reactions. Recently, we have reported the observation of a slowing down in the rates of five different S_N1 hydrolysis reactions at the consolute points of three liquid mixtures. The reactants and solvents were 2-chloro-2-methylbutane (*tert*-amylchloride) in isobutyric acid + water (UCST), 2-chloro-2-methylpropane (*tert*-butylchloride) in isobutyric acid + water, 2-bromo-2-methylpropane (*tert*-butylbromide) in triethylamine + water (LCST), 3-chloro-3-methylpantane in 2-butoxyethanol + water (LCST), and 4-methylbenzyl bromide in 2-butoxyethanol + water [2]. In each case, the reaction kinetics were first order.

In this paper, we revisit the hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water [3] by introducing very careful measurements of the specific rate of reaction in the well-stirred liquid in the two-phase region below the critical solution temperature, T_c. Above T_c, we observe slowing down of the reaction rate, but below T_c we find speeding up. These results are of interest when compared with the most recent theories [4], [5], which predict that the occurrence of slowing down depends upon the proper classification and enumeration of the thermodynamic variables determining the position of chemical equilibrium [6], [7].

2. EXPERIMENT

2.1   Experimental Method

The solvent was isobutyric acid (IBA) + water. The isobutyric acid was purchased from Aldrich, while the water was once-distilled from a glass system. The solvent mixture was prepared at the critical composition (38.8 wt % IBA) by weighing. Before addition of the reactant, the critical temperature was $T_c^{\circ} = 26.12$ ˚C. The reaction mixture consisted of 7.75 μL of 2-chloro-2-methylbutane added to 125 mL of solvent. Both reactant and solvent were temperature equilibrated in a 10 L water bath before mixing. The reaction cell was a hand-made Pyrex tube with height 18 cm., diameter 3.5 cm., and volume 180 cm^3. The tube wall was made as thin as possible to facilitate rapid heat transfer.

If we let RCl represent 2-chloro-2-methylbutane, the overall reaction is

$$RCl + HOH \quad \longrightarrow \quad ROH + HCl \tag{1}$$

where ROH is 2-methyl-2-butanol. Since HCl is a strong electrolyte, the rate of the reaction could be followed by observing the build-up of conductivity. The conductivity measurements were made using the immersion probe of a Hanna Instruments model HI 9032 microcomputer controlled conductivity meter. The temperature range of the meter was 0 to 50 ˚C with a conductivity resolution of 0.1 μS. The cell and the probe were held at the desired temperature in the water bath which was controlled by a Philadelphia Roto-Stat differential thermoregulator connected to a Cole Parmer, 115 V Variable Output, Model G-02149-20 Controller. The temperature was sensed with a Model S27929 L180 G(D), Serial No. 1516, platinum resistance thermometer supplied by Minco Products, Inc. The resistance of the thermometer was read using a Hewlett-Packard Model H3458A, 8-1/2 digit multimeter. Over the length of a kinetics run, the temperature of the bath was stable to ± 0.3 mK.

During the course of the reaction, the liquid in the conductance cell was vigorously stirred in order to homogenize the mixture and to guarantee mass transfer equilibrium across any phase boundaries in the case of experiments carried out in the two-phase region. The temperature

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compensation feature of the Hanna instrument was used to eliminate the effects of temperature fluctuations and also to remove the effect of background conductivity from the measured values.

In general, the addition of a third component to a binary liquid mixture shifts the critical temperature [8], [9]. If the third component is more soluble in one of the original components than the members of that pair are in each other, the region of binary miscibility shrinks. This is reflected by an increase in an UCST and a decrease in an LCST [10].

After the reaction mixture had come to chemical equilibrium, the critical temperature was remeasured by observing the appearance of opalescence and was found to be $T_C = 26.32$ ˚C. Since this represents an increase in the UCST, the combination of the equilibrium concentrations of RCl, ROH, and HCl had the effect of decreasing the miscibility of isobutyric acid + water mixture. For the purposes of illustration, we show in Fig. 2, how the value of T_C measured at chemical equilibrium depended upon the initial concentration of RCl. Nevertheless, because each kinetics run was started with the same initial amounts of solvent and reactant, and the reaction went essentially to completion, the equilibrium critical temperature of 26.32 ˚C could be treated as a constant for the system.

2.2 Data Analysis

Consider a general chemical reaction

$$\nu_1(1) + \nu_2(2) + \nu_3(3) + ... \rightleftharpoons 0 \tag{2}$$
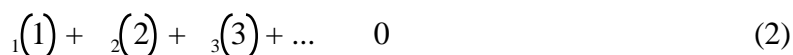
involving the species (1), (2), etc., some of which may be ions. When the species (i) is a reactant, the stoichiometric coefficient $\nu_i > 0$, while when (i) is a product $\nu_i < 0$. If c_i^o is the initial molar concentration of (i), then its concentration at later time is $c_i^o - \nu_i \xi$, where ξ is the extent of reaction (reaction variable). Let λ_i be the molar conductance of (i), and let κ_s be the conductivity of the solvent. The instantaneous conductivity, κ, of the reaction mixture is then

$$\kappa = \kappa_s + \sum_i \left(c_i^o - \nu_i \xi \right) \lambda_i \tag{3}$$

When at the start of the reaction $=0$, the conductivity is $^{\circ}=\ _s+\ _i c^{\circ}_i\ _i$. At reaction equilibrium when $=\ _e$ and the c_i assume their equilibrium values, $c^e_i=c^{\circ}_i-\ _{i}\ _e$, the conductivity is $^e=\ _s+\ _i c^e_i\ _i$. Since $_i/\left(c^{\circ}_i - c^e_i\right)=1/\ _e$ is the same for all i (same for each species), Eq. (3) can be converted to

$$= \ ^{\circ}+\frac{\left(\ ^e-\ ^{\circ}\right)\ _i}{c^{\circ}_i - c^e_i} \tag{4}$$

which is the basic result for the conductivity of reacting mixtures.

The kinetics of the reaction in Eq. (1) are first order in the concentration of RCl. Since equilibrium lies far to the right, the reaction goes essentially to completion and

$$=c^{\circ}_{RCl}\left(1 - e^{-t/}\right) \tag{5}$$

where c°_{RCl} is the initial concentration of RCl, and the relaxation time, , is related to the first order rate constant, $k=1/$.

To apply Eq. (4), we let (i) = HCl. The initial concentration is $c^{\circ}_{HCl}=0$, while since the reaction goes essentially to completion, the equilibrium concentration is $c^e_{HCl}-c^{\circ}_{RCl}$. Because HCl is a product, $_{HCl}=-1$. The initial conductivity is $^{\circ}$. Substituting these results and Eq. (5) into Eq. (4) gives

$$= \ ^{\circ}+\left(\ ^e-\ ^{\circ}\right)\left(1 - e^{-t/}\right) \tag{6}$$

The software of the Hanna conductivity meter compensated for $^{\circ}$; hence, the difference, $-\ ^{\circ}$ predicted by Eq. (6) was fitted to the data from each run with $^e-\ ^{\circ}$ and $1/$ taken as adjustable parameters.

In Fig. 3, we show an Arrhenius plot of the temperature dependence of $1/$. The straight line is given by the equation

$$\ln\left(1/\ \right)=43.0 - 116{,}100/RT \tag{7}$$

The units of are min., R is the gas law constant, T is the absolute temperature, and the units of the coefficient of 1/RT are J / mole. The values of the coefficients in Eq. (7) were obtained by

fitting the Arrhenius equation to data obtained in the one-phase region of the mixture at temperatures far above T_C. The activation energy (116.1 kJ / mole) was somewhat higher than we found previously for this system [3]. Eq. (7) forms the "background" against which the size of critical effects can be judged. It is apparent from the figure that the specific rate of reaction slows down in the one-phase region above T_C and speeds up in the two-phase region below it.

In our previous study of this reaction [3], we did not have enough data to distinguish the region of speeding up from background, and we located the critical temperature, T_c, near the minimum of the slowing down region. Because we also used a large initial concentrationof RCl, T_c was many degrees above T_c^o. By contrast, in the experiments we have just described, so little RCl was required that T_c and T_c^o differed by less than the width of the critical region (about 1˚C).

Snyder and Eckert measured the rate of reaction of isoprene with maleic anhydride near the UCST's of hexane + nitrobenzene and hexane + nitroethane, and in both instances, observed only speeding up [11]. This is the only other case of speeding up of reaction rates in liquid mixtures that has come to our attention.

3. THEORY

3.1 Kinetics

As an S_N1 reaction, the hydrolysis of 2-chloro-2-methylbutane can be represented by the simple mechanism

$$RCl \qquad R^+ \ + \ Cl^- \qquad\qquad (8)$$

$$R^+ + HOH \qquad ROH \ + \ H^+ \qquad\qquad (9)$$

where the first step is rate-controlling. Eq. (8) goes essentially to completion; nevertheless, since our object is to relate the kinetics to the thermodynamics, we should consider this first step as reversible and express the rate of reaction in terms of $_e$.

Equilibrium in the second step is reached quickly and lies far to the right. The molar concentrations, c_{R^+}, c_{ROH}, c_{H^+}, of the species R^+, ROH, and H^+, respectively, are related by

$$K_R = \frac{c_{ROH}c_{H^+}}{c_{R^+}} \tag{10}$$

where since the thermodynamic activities are not considered explicitly, K_R, is not an equilibrium constant but is an equilibrium concentration ratio. The extent of reaction, , may be set equal to c_{Cl^-}, and because the concentration of R^+ is very small, we have also $- c_{ROH} = c_{H^+}$. These results permit Eq. (10) to be solved for

$$c_{R^+} = {}^2/K_R \tag{11}$$

We next let k and k be the rate coefficients for reaction in the forward and reverse directions in Eq. (8). Since Eq. (8) is rate controlling, the rate law is

$$\frac{dc_{RCl}}{dt} = - k\ c_{RCl} + k\ c_{R^+}c_{Cl^-} \tag{12}$$

Using $c_{RCl} = c_{RCl}^o - $ and Eq. (11), Eq. (12) becomes

$$\frac{d}{dt} = k\ \left(c_{RCl}^o - \right) - \frac{k\ {}^3}{K_R} \tag{13}$$

The equilibrium value, ${}_e$, of the reaction variable is obtained by setting the right hand side of Eq. (13) to zero. Since the equilibria in both Eqs. (8) and (9) lie far to the right, and $k\ \left(c_{RCl}^o \right)^2/k\ K_R << 1$, we can then solve the resulting cubic equation to lowest order using perturbation theory [12] to obtain

$${}_e = c_{RCl}^o\left(1 - k\ \left(c_{RCl}^o \right)^2/k\ K_R \right) \tag{14}$$

Being a function of , the right hand side of Eq. (13) can be expanded in a Taylor series about $= {}_e$; because the higher derivatives are zero, this series has only three terms,

$$\frac{d}{dt} = - k\left(1 + \frac{3k\ {}_e^2}{k\ K_R} \right)(- {}_e) - \frac{3k\ {}_e}{K_R}(- {}_e)^2 - \frac{k}{K_R}(- {}_e)^3 \tag{15}$$

Substituting Eq. (14) into Eq. (15) and collecting terms of lowest (actually zeroth) order in $k\ \left(c_{RCl}^o \right)^2/k\ K_R$, we obtain

$$\frac{d}{dt} = - k(- {}_e) \tag{16}$$

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Because of Eq. (14), we have also to lowest order $\xi_e = c^o_{RCl}$. Eq. (16) is the rate law for a reaction which is essentially irreversible. With $k = 1/\tau$, its integral is Eq. (5).

3.2 Thermodynamics

A non-equilibrium thermodynamic analysis [13], [14] of the rate gives to the same degree in $\left(\xi - \xi_e\right)$,

$$\frac{d\xi}{dt} = \frac{-\kappa\, a_{RCl}\left(\xi_e\right)}{y^*\left(\xi_e\right)RT}\left(\frac{\partial G}{\partial \xi}\right)_e\left(\xi - \xi_e\right) \qquad (17)$$

where κ is the rate coefficient for the forward reaction in Eq. (8) in dilute ideal solution, $a_{RCl}\left(\xi_e\right)$ is the thermodynamic activity of RCl evaluated at equilibrium, $y^*\left(\xi_e\right)$ is the equilibrium value of the activity coefficient of the transition state and $\left(\partial G/\partial \xi\right)_e$ is the equilibrium value of the reaction variable derivative of the instantaneous Gibbs free energy difference between products and reactants in Eq. (1) [2]. The factor, $a_{RCl}\left(\xi_e\right)/y^*\left(\xi_e\right)$, can be interpreted as the forward rate of the reaction in Eq. (8) at equilibrium. Since Eqs. (16) and (17) each are representations of the leading terms in Taylor series expansions of the net rate, we can set the coefficients of $\left(\xi - \xi_e\right)$ equal to obtain:

$$k = \frac{\kappa\, a_{RCl}\left(\xi_e\right)}{y^*\left(\xi_e\right)RT}\left(\frac{\partial G}{\partial \xi}\right)_e \qquad (18)$$

4. DISCUSSION AND CONCLUSIONS

If in Eq. (18), we can assume that as $T \to T_c$, there are no critical point effects in the coefficient, $a_{RCl}\left(\xi_e\right)/y^*\left(\xi_e\right)$ [4], [5], then the behavior of k near T_C is determined by the thermodynamic derivative, $\left(\partial G/\partial \xi\right)_e$.

According to Griffiths and Wheeler [15], the analysis of the critical behavior of $\left(\partial G/\partial \xi\right)_e$ begins with the separation of the thermodynamic variables into two classes: In the first class are the "fields", such as temperature, pressure, and component chemical potentials. A field has the same value in each phase coexisting in equilibrium. As an example, at thermal equilibrium, the temperature must be the same in each phase. In the second class are the "densities", such as entropy and the concentrations of chemical components, which have different

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values in each coexisting phase. A solute, for example, will in general have a different solubility in each of two coexisting liquid phases.

Griffiths and Wheeler argue that when the experimental conditions are such that only fields and two or more densities are held fixed, the value of the derivative of a field with respect to a density, of which $\left(\partial G/\partial\xi\right)_e$ is a case in point, will not change abruptly at temperatures T near T_C. If fewer than two densities are held fixed, however, then $\left(\partial G/\partial\xi\right)_e \sim \left(\left|T - T_c\right|/T_c\right)^x$ for T near T_C. If one density is held fixed, $\left(\partial G/\partial\xi\right)_e$ is said to go to zero "weakly" in the sense that x involves one of the small critical exponents, either $\alpha = 0.11$ [16] (α determines the temperature dependence of the constant volume specific heat of a pure fluid) or $\beta = 0.332$ [16] (β determines the shape of the liquid-vapor coexistence curve of a pure fluid). If no densities are held fixed, $\left(\partial G/\partial\xi\right)_e$ is said to go to zero "strongly" in the sense that x involves one of the large critical exponents, either $\gamma = 1.24$ [16] (γ determines the temperature dependence of the isothermal compressibility of a pure fluid) or $\delta = 4.9$ [16] (δ determines the shape of the critical isotherm of a pure fluid).

For a reaction in a thermostat open to the atmosphere, the appropriate field variables are presumably the pressure, P, and the temperature, T. As composition variables (densities), we choose mass fractions as opposed to mole fractions [2], [3], because chemical reactions conserve mass but not moles. Use of mass fractions and mass conservation makes it easy to determine which, if any, of the composition variables are held fixed during the course of a reaction. In the case of our experiment, the appropriate composition variables are the mass fractions w_{IBA}, w_{HOH}, w_{RCl}, w_{ROH}, and w_{HCl} of the components isobutyric acid (IBA), water, RCl, ROH, and HCl, respectively. If we can assume that isobutyric acid is inert, then w_{IBA}, T and P are held fixed. Because of the chemical reaction connecting them, the mass fractions of the other components at equilibrium depend upon T and P and possibly also w_{IBA}. With one density w_{IBA} fixed, we conclude that $\left(\partial G/\partial\xi\right)_e$ should go to zero "weakly," and the kinetics of the reaction should slow down as T $\rightarrow$ T_c. On the other hand, isobutyric acid is known to react with alcohols, such as ROH, to form esters. This event would introduce the mass fraction of the ester as a new

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composition variable and would at equilibrium make both this variable and w_{IBA} functions of T

and P. Under these conditions, no density would then be held fixed, and we should expect

$\left(\partial G/\partial \xi \right)_e$ to go to zero "strongly"; the kinetics of the hydrolysis reaction should again slow

down as $T \to T_c$. Thus whether IBA is inert or not, the application of Griffiths and Wheeler rules

to Eq. (18) implies that the rate of hydrolysis of RCl should be slowed as is illustrated by the data

in Fig. 3 at least for temperatures $T > T_c$.

By contrast, Milner and Martin [5] argue that the model of homogeneous kinetics implied

by Eqs. (16) - (18) is unsatisfactory, because it ignores the coupling between the fluctuations in

the thermodynamic variables that take place near a critical point. Because these fluctuations are

long range as $T \to T_c$, Milner and Martin suggest that the kinetics are better represented by the

equations of linearized hydrodynamics. This system of equations includes three sound modes

(two transverse and one longitudinal), a heat relaxation mode, and a chemical relaxation mode.

Since the mode with the slowest rate of decay will determine the critical slowing down, Milner

and Martin reject the three rapidly decaying sound modes in favor of the thermal and chemical

modes. The decay of these two modes occurs by the interplay of chemical reaction with the

diffusion of entropy and concentration. These effects can be represented in time and space by a

pair of coupled partial differential equations, which can be solved to obtain the spatial normal

modes and the temporal decay constants. Exactly which spatial normal modes are encountered in

practice depends upon the boundary values and initial conditions satisfied by the entropy and the

composition variables.

Because there are two coupled equations, each spatial normal mode is associated with two

temporal decay constants. In analyzing the critical behavior of these constants, we shall assume

that the mixture contains no inert chemical components. This makes the arguments appropriate to

the case where we have taken into account the separate reaction between ROH and IBA to form

an ester. According to Milner and Martin, the values assumed by the two decay constants fall into

two regimes of behavior depending upon the wavelength of the normal mode. Regime I: For

normal modes of long wavelength, the two decay constants are proportional to (in our notation)

$\left(\partial T / \partial S \right)_G$ and $\left(\partial G / \partial \mu \right)_S$, respectively. Since G is a field, and the entropy, S, is a density, the first of these derivatives should go to zero "strongly", while the second should go to zero "weakly". Regime II: For normal modes of short wavelength, the decay constants are proportional to $\left(\partial G / \partial \mu \right)_T$ and $\left(\partial T / \partial S \right)_\mu$, respectively. The first of these should go to zero "strongly". The second should go to zero "weakly", since μ is a density. Both of these decay constant regimes are qualitatively consistent with the slowing down observed in Fig. 3 for $T > T_c$.

Strictly speaking, Milner and Martin analyze in detail only a binary fluid with an isomerization reaction linking the components. Their conclusions appear to be general, however, so we have applied their picture to our more complex case.

Neither Eq. (18) nor the hydrodynamic model of Milner and Martin would seem to be consistent with the speeding up in reaction rate evident in Fig. 3 for $T < T_c$, since both theories rely upon thermodynamic derivatives which approach zero as $T \rightarrow T_c$. Below T_c, two phases coexist, and because of the strong stirring, the measured reaction rate may in fact be some composite of the individual rates prevailing in each phase. Indeed, all three chemical factors, γ, $a_{RCl}\left(\mu_e \right)$, and $y^*\left(\mu_e \right)$ in Eq. (18) are likely to have different values in each phase, which implies that so also must k. This holds out the possibility that rate observed in the region $T < T_c$ may be only incidently related to the critical point.

ACKNOWLEDGMENTS

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CAPTIONS

Fig. 1 Liquid-liquid phase boundary curves for a mixture of components A and B. The mole fraction of A is X_A , and the temperature is T. The drawing on the left illustrates an upper critical solution temperature, T_c , while the one on the right illustrates a lower critical solution temperature. In both cases, a single liquid phase is present on the convex side of the curve, whereas two liquids are present on the concave side. The (X_A, T) coordinates of the extremum define the consolute point.

Fig. 2 Equilibrium critical temperature, T_c , for solutions of 2-chloro-2-methylbutane in 38.8 weight % isobutyric acid + water as a function of the initial concentration of 2-chloro-2-methylbutane. The two plotting symbols represent measurements made starting with different batches of isobutyric acid + water.

Fig. 3 Arrhenius plot of the relaxation rate, 1 /   , for the hydrolysis of 7.75 µL of 2-chloro-2-methylbutane in 125 mL of the mixture 38.8% isobutyric acid+ water. The reciprocal of the absolute temperature is 1/T, while the reciprocal of the equilibrium critical temperature is located by the symbol T_c . This temperature corresponds to 26.32 ˚C.
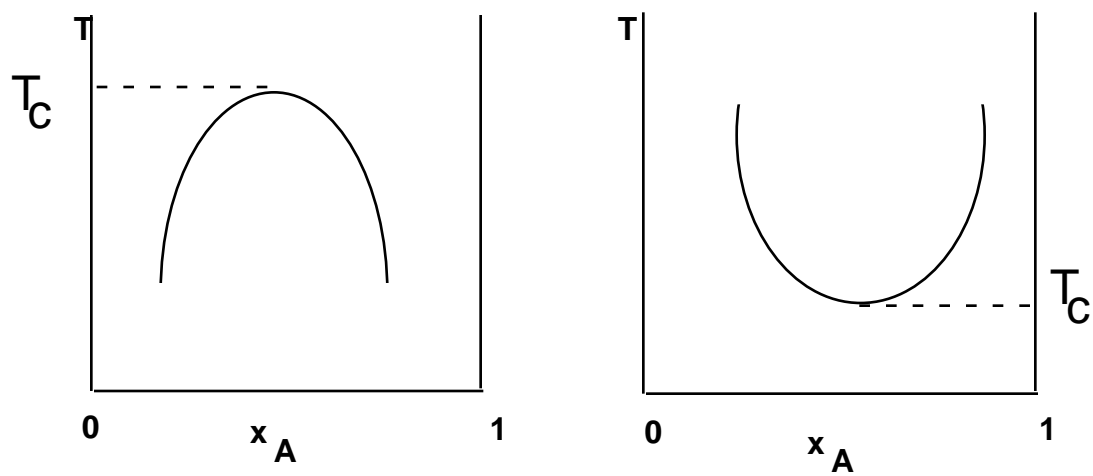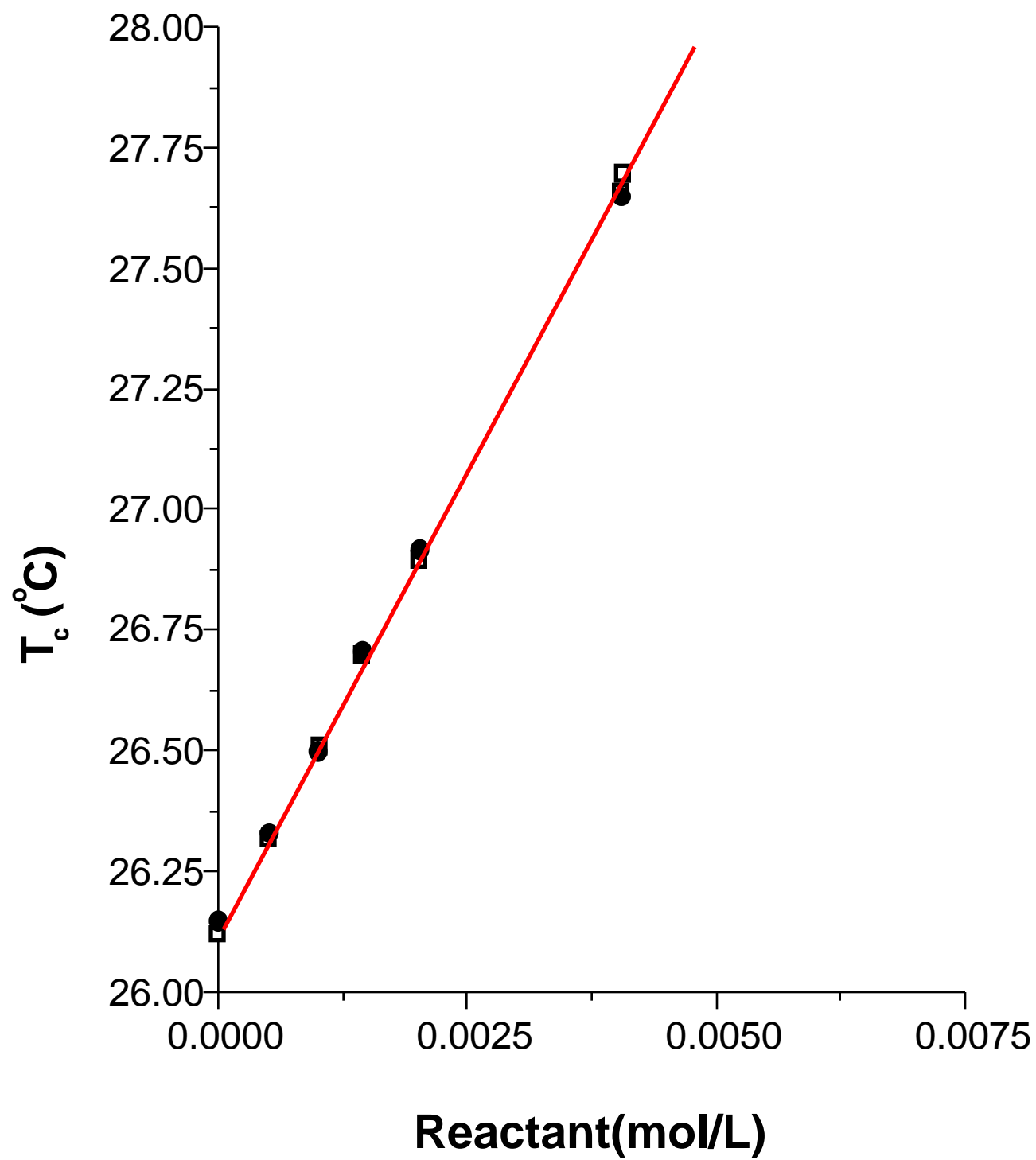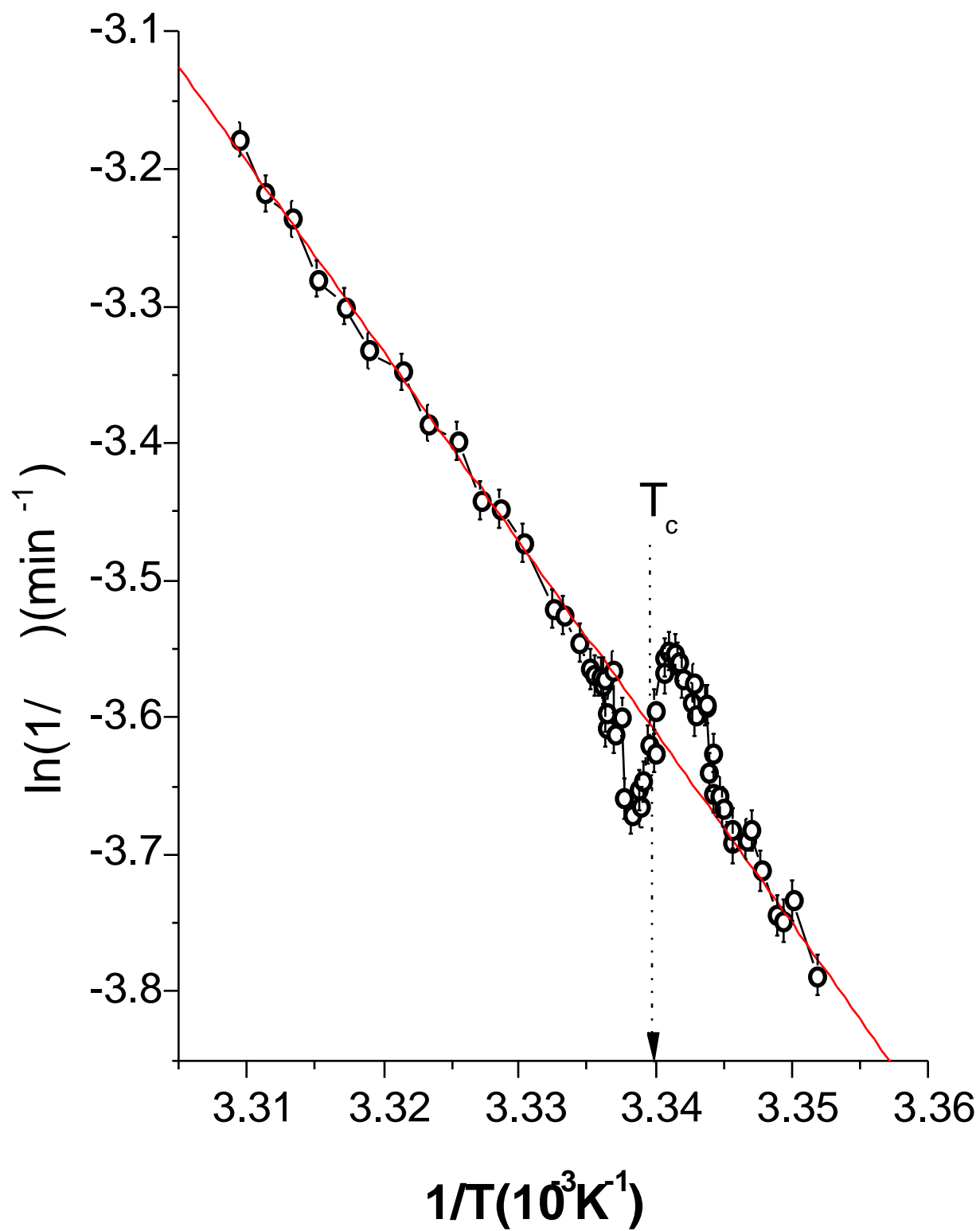
Fig. 1

Fig. 2

Fig. 3